K-979

UNITED STATES ATOMIC ENERGY COMMISSION

THE VAPOR PRESSURE OF A MIXTURE OF H_2O AND D_2O

By
C. F. Hale
George D. Oliver

November 24, 1952

K-25 Plant
Carbide and Carbon Chemicals Company
Oak Ridge, Tennessee

Date Declassified: January 5, 1956.

This report has been reproduced directly from the best
available copy.

Issuance of this document does not constitute authority
for declassification of classified material of the same or
similar content and title by the same authors.

Printed in USA, Price 15 cents. Available from the
Office of Technical Services, Department of Commerce, Wash-
ington 25, D. C.

THE VAPOR PRESSURE OF A MIXTURE OF H_2O AND D_2O

C. F. Hale and George D. Oliver

Work Supervised by
H. A. Bernhardt
Laboratory Division
F. W. Hurd, Superintendent

Date of Issue: November 24, 1952

ABSTRACT

The vapor pressure of a 50-50 mole % mixture (HDO) of H_2O and D_2O and the difference in pressure of H_2O and HDO from 160 to 3143 psia. have been determined by means of a high pressure ebulliometer. A plot of the data shows the vapor pressures of H_2O, D_2O, and HDO to be equal at 220.7°C. and 340.9 psia. The vapor pressure of HDO is an average of that of H_2O and D_2O.

Work performed under Contract No. W-7405-Eng-26

CARBIDE AND CARBON CHEMICALS COMPANY
UNION CARBIDE AND CARBON CORPORATION
K-25 Plant
Oak Ridge, Tennessee

THE VAPOR PRESSURE OF A MIXTURE OF H_2O AND D_2O

A recent report by Oliver, Grisard and Milton (2) presented the vapor pressure data on pure D_2O and the difference in pressure of D_2O and H_2O from 200 psia. to the critical point. In exploring the possibilities of producing heavy water by distillation at high temperatures, the vapor pressure of a 50 mole % mixture of D_2O and H_2O has now been measured from about 150 to 3000 pounds. Since the first report gave a short review of the vapor pressure and critical constants data found in the literature, only the experimental data on the mixture will be considered here.

EXPERIMENTAL

Material

The D_2O was the same as that used in the previous work: conductivity, 2.7×10^{-6} mhos; pH, 6.5; weight % D_2O, 99.87. Heavy water from Trail, British Columbia, the source of this sample, normally contains about 0.3% of the O^{18} isotope. The sample of normal water was doubly distilled with the second distillation being made from a permanganate solution. In preparing the 50-50 mole % mixture, the amount of D_2O in normal water (0.0147 mol %) and the weight % D_2O, 99.87, of the heavy water, were used in calculating the weights of material. Using molecular weights for D_2O of 20.0283 and for H_2O of 18.0157, the composition of the sample placed in the boiling point tube was calculated to be 50.33 mol % D_2O and 49.67 mol % H_2O.

Apparatus and Procedure

All apparatus used in this investigation was the same as that described previously (2). Briefly, the apparatus was composed of two boiling point tubes connected through traps to a common pressure system containing helium. The boiling temperature of the HDO in one tube was compared directly with the boiling temperature of normal water in the other. A platinum thermohm and G-2 Mueller bridge with accessory equipment were used to measure temperatures. The system pressure corresponding to the observed boiling point of the normal water was obtained from steam tables.

RESULTS AND DISCUSSION

It has been assumed that the vapor pressure of a 50-50 mole % mixture of D_2O and H_2O would be an average of the vapor pressure of each compound. Of course, this postulation was based on the assumption that an ideal solution is formed by mixing D_2O and H_2O.

Boiling point measurements were made on H_2O and HDO over the pressure range of 150 to 3000 psia. These data and the difference in the boiling points at each observed pressure are listed in table I. Using the data of table I and the previous work (2), a plot was made of the boiling point difference between H_2O and D_2O, and H_2O and HDO. This plot, figure 1, shows the boiling points of the 50-50 mole % mixture, HDO, to be an average of those for the
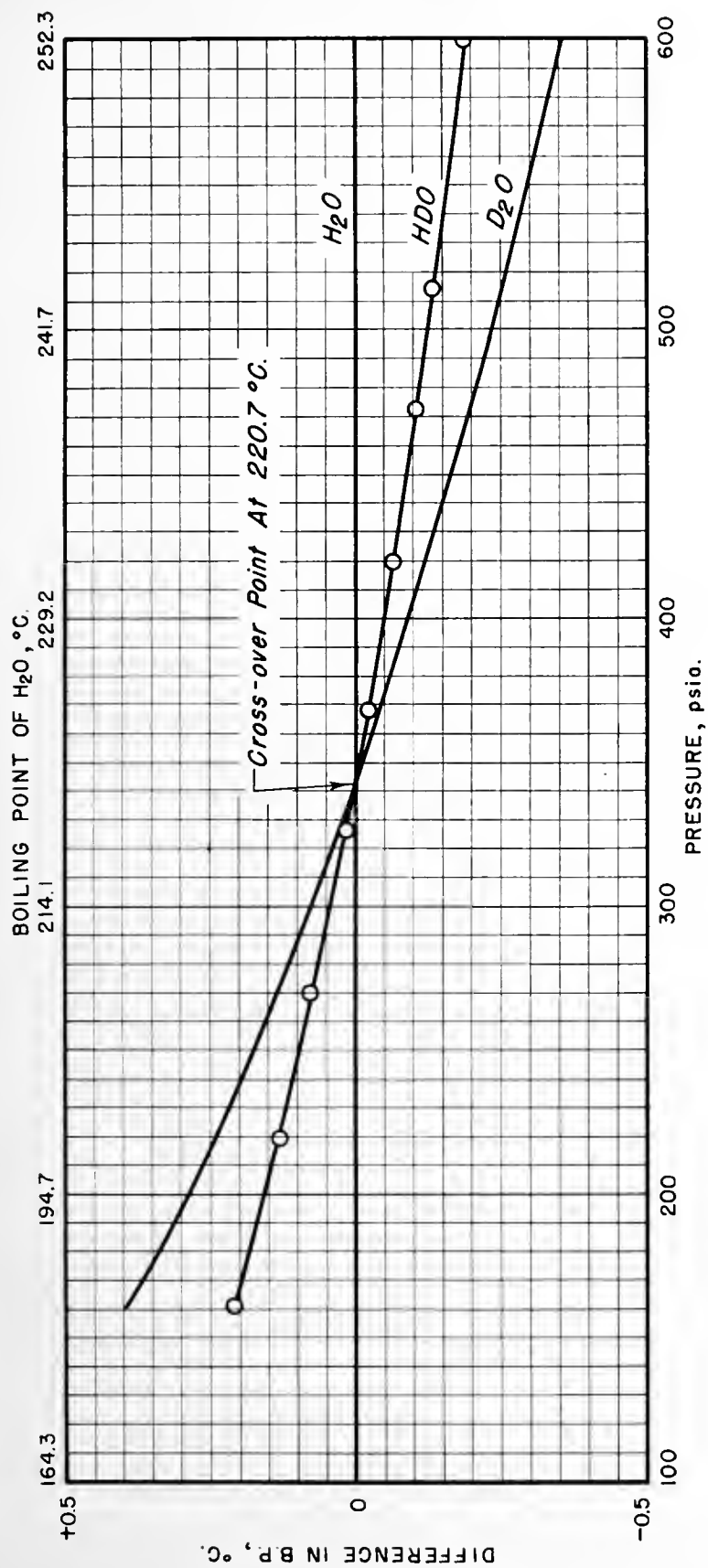
DIFFERENCE IN BOILING POINTS OF
H_2O, D_2O, AND HDO

FIGURE 1

pure materials. Moreover, the three curves cross at the same point of temperature, 220.7°C., and pressure, 340.9 psia. Therefore, it may be concluded that D_2O and H_2O form an ideal solution over the entire liquid range. The data obtained above 3000 psia. indicate that the critical point for HDO lies between the critical points of H_2O and D_2O.

TABLE I

VAPOR PRESSURE OF H_2O AND HDO

Pressure, psia.	Boiling Points, t°C.		ΔT (H_2O - HDO), °C.
	H_2O	HDO	
161.36	184.57	184.78	-0.216
219.40	198.68	198.81	-0.132
265.85	208.00	208.08	-0.084
325.97	218.34	218.36	-0.023
367.54	224.66	224.64	0.018
420.51	231.95	231.89	0.058
472.14	238.41	238.31	0.102
514.24	243.28	243.15	0.126
619.38	254.24	254.05	0.187
1607.7	318.62	318.09	0.532
3017.5	369.01	368.04	0.969
3143.3	372.42	371.26	1.164
3144.1	372.45	371.29	1.152

BIBLIOGRAPHY

1. Kirshenbaum, I., *Physical Properties and Analysis of Heavy Water*, First Ed., New York, McGraw-Hill, 1951, p. 396.

2. Oliver, G. D., Grisard, J. W., Milton, H. T., *The Vapor Pressure of D_2O and Vapor Pressure Difference of D_2O and H_2O, From 200 to 374°C.*, Carbide and Carbon Chemicals Company, K-25 Plant, March 12, 1952 (K-874).

NOTEBOOK REFERENCES

Oliver, G. D., K-25 Notebook No. 1764, p. 57 - 85.

Experimental work completed November 3, 1952.